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On the Surface Free Energy of the Crystallites in Drawn Polyethylene*

AS OBSERVED by some investigators[1-3] the melting point of drawn linear polyethylene is almost independent of the preparation and annealing conditions and also of the crystal thickness. With single crystals and melt crystallized polyethylene, on the other hand, a linear relationship between the reciprocal value of crystal thickness and melting point has been found in agreement with the Thomson equation. In the light of a model proposed by Fischer, Goddar and Schmidt[4,5] there seems to be a possibility of understanding the constancy of the melting point of drawn polyethylene.

The model mentioned above starts from the assumption that the structure of the unannealed drawn polymer is represented by a nearly homogeneous crystalline matrix with high defect concentration caused by chain folds, chain ends, and disarranged sequences. As a consequence of the annealing treatment the defects diffuse to the boundaries of the crystalline regions and a layer structure is created. To describe the thermal behaviour of the polymer, knowledge of the surface free energy between the crystalline and disordered regions is necessary. It is quite clear that this quantity depends on the colloidal structure of the polymer. Using a two-phase model the surface free energy, σ_e, can be calculated according to the Thomson equation

$$\sigma_e = \{(T_m^0 - T_m)/2\,T_m^0\}\,\Delta h\,l \qquad (1)$$

where T_m^0 is the equilibrium melting point, T_m the actual melting point, and Δh represents[6,7] the heat of fusion per volume unit (2.93×10^9 erg/cm³). The crystal thickness, l, is given by the expression

$$l = \alpha\,L \qquad (2)$$

Here L means the long period, and α signifies the degree of crystallinity which may be estimated from density or enthalpy measurements. Because of the difficulties in calculating the degree of crystallinity of drawn polyethylene (for further information see refs 5 and 6) this quantity was taken to be constant and a reasonable value of 0.85 was chosen. A deviation

of this value in the range of 0·05 has negligible influence on the calculated amounts of surface free energy, see *Table 1*.

Table 1. Physical properties of drawn polyethylene

Draw temp. (°C)	Anneal. temp. (°C)	Anneal. time (h)	Melting point (°C)	Long period (Å)	Density (g/cm³)	Crystal- linity (%)	Crystal thickn. (Å)	Surface free energy* (erg/cm²) (1)	(2)
70	unann.	—	136·0	186	0·962	85±5	158±9	29±2	49±3
,,	110	1	136·0	208	0·971	,,	177	32	54
,,	119	,,	136·4	245	0·972	,,	208	35	60
,,	125	,,	136·3	279	0·973	,,	237	40	70
,,	128	,,	136·6	299	0·973	,,	254	41	72
,,	130	,,	136·6	314	0·9	,,	267	43	76
,,	132	,,	136·8	360	0·970	,,	306±18	47±3	85±4
,,	113	200	136·9	242	0·974	,,	206	30	56
,,	120	,,	137·2	280	0·975	,,	238	33	62
,,	125	,,	137·5	310	0·977	,,	264	34	67
,,	128	,,	137·5	340	0·977	,,	289	37	73
,,	130	,,	137·8	360	0·976	,,	306	36	74
,,	131	,,	137·9	372	0·975	,,	316	36	75
80	unann.	—	133·4	196	0·960	,,	167	46	65
,,	125	1	133·2	303	0·968	,,	251	72	104

*(1) Calculated with $T_m^0 = 141·1\,°C$; (2) Calculated with $T_m^0 = 144·7\,°C$.

Measurements were carried out as follows: High density polyethylene (Type 6011 L from BASF) was drawn at 70°C or 80°C and annealed at various temperatures between 110°C and 132°C for 1 h or 200 h. Long periods were detected by a Kratky camera; densities were measured using a density gradient column. Thermal measurements were performed with DTA equipment described elsewhere[6]. The results of all measurements are summarized in *Table 1*. For the equilibrium melting point of polyethylene
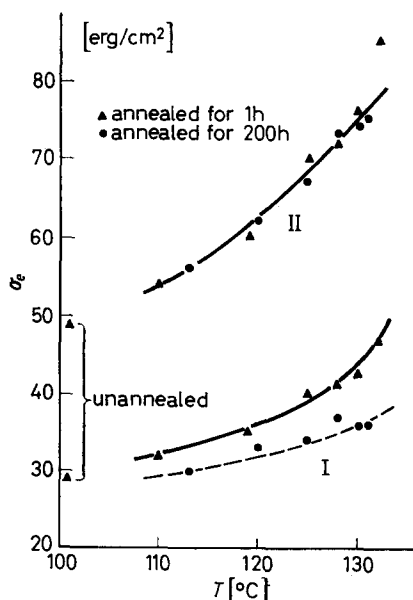

Figure 1—Dependence of surface free energy σ_e of drawn polyethylene (6011 L) on annealing temperature and time: I: Calculated with $T_m^0 = 141·1\,°C$; II: Calculated with $T_m^0 = 144·7\,°C$

two different values ($141 \cdot 1°C^8$ and $144 \cdot 7°C^9$) are reported. Therefore σ_e was calculated for both values. The data are listed in *Table 1* and plotted in *Figure 1* as a function of annealing temperature. In this context the correctness of the reported equilibrium melting points will not be discussed. As shown in *Figure 1* the surface free energy increases with annealing temperature. The value of σ_e depends slightly on the annealing time and strongly on the value which is adopted for T_m^0. Using the lower value of the equilibrium melting point the surface free energy reaches 35 to 45 erg/cm^2 for a sample annealed at about 130°C. The higher value of the equilibrium melting point yields 75 to 80 erg/cm^2 for the same sample. This latter result is in good agreement with data obtained by different investigations on polyethylene single crystals and melt crystallized material[4, 10–12].

The increase of σ_e can be understood with the aid of the cited model. The surface free energy grows as a consequence of the structural changes taking place during annealing which are connected with the forming of a layer structure of crystalline and amorphous regions. Looking at the melting point of drawn polyethylene this quantity may be constant because increases in crystal thickness are offset by accompanying increases in surface free energy.

Although the value of the equilibrium melting point and therefore the amount of the surface free energy is not determined definitely the increment of the surface free energy with annealing temperature and the constancy of the melting point of drawn polyethylene can be explained with respect to the model described above.

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